

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

Publication number:

**0 494 422 A2**

(12)

## EUROPEAN PATENT APPLICATION

- (21) Application number: **91121842.8**
- (51) Int. Cl.<sup>5</sup>: **C08L 67/00, C08K 13/04, A47J 36/04, //(C08L67/00,27:18)**
- (22) Date of filing: **19.12.91**

(30) Priority: **08.01.91 JP 435/91**

(43) Date of publication of application:  
**15.07.92 Bulletin 92/29**

(84) Designated Contracting States:  
**DE FR GB NL**

(71) Applicant: **SUMITOMO CHEMICAL COMPANY, LIMITED**  
**5-33, Kitahama 4-chome Chuo-ku**  
**Osaka(JP)**

(72) Inventor: **Asai, Kuniaki**  
**8-8, Tanigawacho**  
**Tondabayashi-shi(JP)**  
Inventor: **Kobayashi, Tadayasu**  
**12-19-206, Ninomiya-1-chome**  
**Tsukuba-shi(JP)**  
Inventor: **Maeda, Mituo**  
**40-1, Kasuga-2-chome**  
**Tsukuba-shi(JP)**

(74) Representative: **Henkel, Feller, Hänzel & Partner**  
**Möhlstrasse 37**  
**W-8000 München 80(DE)**

(54) **Wholly aromatic polyester resin composition and ovenware obtained by moulding said composition.**

(57) **A wholly aromatic polyester resin composition contains:**

- (1) a wholly aromatic polyester resin,
- (2) at least one member selected from a glass fiber and a silica-alumina fiber,
- (3) glass beads,
- (4) titanium oxide, and
- (5) a fluorocarbon polymer.

The wholly aromatic polyester resin composition has high heat resistance and mechanical strengths, low anisotropy and excellent appearance, and shows low dissolution of components, excellent releasability and non-tackiness. It can be molded into an ovenware.

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## FIELD OF THE INVENTION

The present invention relates to a wholly aromatic polyester resin composition having high heat resistance and mechanical strengths, low anisotropy [anisotropy refers to the difference in properties of melt between machine direction and transverse direction], excellent appearance, low dissolution in an extraction test according to No. 20 of the Welfare Ministry, excellent releasability and non-tackiness, as well as to an ovenware obtained by molding said composition.

## DESCRIPTION OF RELATED ART

Certain plastic materials, for example, polymethylpentene and polysulfone are in use as a cooking vessel for microwave oven.

Ovenwares, i.e. cooking vessels for microwave oven with electric range, capable of effecting microwave irradiation and electric heating, are required to be excellent in various properties such as heat resistance, electrical properties, chemical resistance, appearance and the like. They are required to show a very high performance particularly in heat resistance because they not only undergo heat generation by microwave irradiation but also are exposed to the heat generated by electric range. For example, they are required to show no deformation and retain practical mechanical properties even at 200°-250° C.

Wholly aromatic polyester resins have various excellent properties due to the molecular structure and outperform all other resins in heat resistance in particular. Of the wholly aromatic polyester resins, those produced from (a) terephthalic acid or isophthalic acid, (b) parahydroxybenzoic acid or its derivative and (c) 4,4'-dihydroxydiphenyl or its derivative are injection-moldable and excellent in various properties such as heat resistance, chemical resistance, oil resistance, radiation resistance, insulation and the like, and accordingly find wide applications in electric, electronic and other fields. Examples of the applications are motor parts (commutator, brush holder), hair drier grill, lamp holder, relay parts, printed circuit board, connector, bobbin, IC device parts (IC socket, sleeve, wafer basket, etc.), thermistor case, heat sealer parts and jig for canning. Further, they have a high crystallinity and a very high heat distortion temperature of 250° C or more although they have a high dielectric loss tangent (0.004-0.02 similarly to conventional polyester resins). Accordingly, even when irradiated with a microwave, they remain at temperatures lower than the heat distortion temperature and do not undergo easy deformation. Therefore, they have a heat resistance suitable for use as an ovenware.

However, said aromatic polyester resins show liquid crystal property in a molten state and, when they are injection-molded, the molded articles are significantly oriented to the machine direction (hereinafter referred to as MD) of the melt. Therefore, the molded articles have a large difference in mold shrinkage between MD and a direction transversing the MD (hereinafter referred to as TD) [(mold shrinkage in TD)/(mold shrinkage in MD) is larger than 10]. Accordingly, they have large mechanical strengths in the orientation direction but small strengths in a direction transversing the orientation direction. Thus, the molded articles show a high anisotropy. Further, the molded articles have no beautiful appearance due to the nonuniform flow marks. Accordingly, when said wholly aromatic polyester resins are molded into relatively large shapes such as ovenware, the molded articles tend to cause warpage and give no comfortable appearance.

In order to solve the above-mentioned problems of wholly aromatic polyester resins, it has hitherto been studied to incorporate fibrous reinforcing agents and fillers into the resins. When a fibrous reinforcing agent such as glass fiber is incorporated, improvement in rigidity and reduction in mold shrinkage are seen depending upon the amount of the agent added; however, improvement in anisotropy is low and no improvement in appearance is obtained. JP-A-1-165667 discloses a composition obtained by incorporating a glass fiber and titanium oxide into a wholly aromatic polyester resin. In this composition, slight improvement in appearance is seen according to the addition of titanium oxide but improvement in anisotropy is insufficient.

JP-A-60-124649 discloses a composition obtained by incorporating talc and titanium oxide into a wholly aromatic polyester resin. Although this composition has significantly improved appearance and anisotropy without sacrificing the flowability of the wholly aromatic polyester resin, it has greatly reduced mechanical strengths, particularly greatly reduced impact strength. Therefore, the composition has an insufficient strength when molded into an ovenware.

USP 4,585,823 discloses an ovenware obtained by molding a composition comprising a wholly aromatic polyester resin, wollastonite and titanium oxide. Although this composition has high mechanical strengths, low anisotropy and excellent appearance, it shows a very high dissolution amount of solubles in an aqueous acetic acid solution (larger than 500 ppm). The dissolution amount is the amount of an evaporation residue

when the ovenware is subjected to an extraction test according to No. 20 of the Welfare Ministry. In this test, the ovenware is immersed in a 4% aqueous acetic acid solution at 121 °C for 120 minutes and the evaporation residue of the resulting solution is measured. Accordingly, the composition is not desirable for use as cooking vessels, for example, an ovenware. The above very high dissolution amount is caused by the dissolution of wollastonite present in the composition, in 4% acetic acid.

## SUMMARY OF THE INVENTION

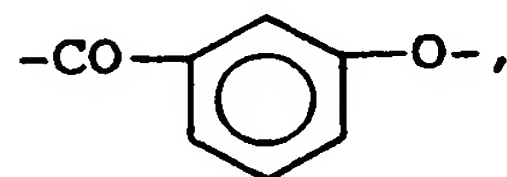
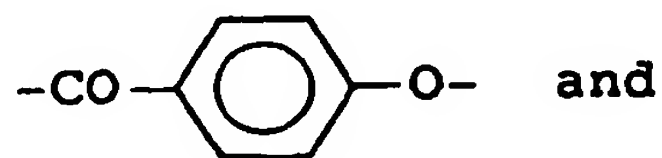
It is an object of the present invention to provide a wholly aromatic polyester resin composition having high heat resistance and good mechanical strengths, low anisotropy, excellent appearance, low dissolution in an extraction test according to No. 20 of the Welfare Ministry, excellent releasability and non-tackiness, as well as an ovenware obtained by molding said composition.

The present inventors made study in order to solve the above-mentioned problems of the prior art and, as a result, found that a composition meeting the above requirements can be obtained by incorporating into a wholly aromatic polyester resin specific amounts of (a) at least one fibrous reinforcing agent selected from the group consisting of a glass fiber and a silica-alumina fiber, (b) glass beads, (c) titanium oxide and (d) a fluorocarbon polymer having a specific structure and that a molded article obtained from the composition has excellent properties suitable for use as an ovenware. The above finding has led to the completion of the present invention.

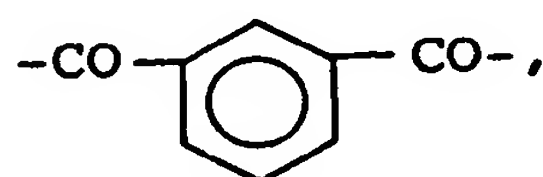
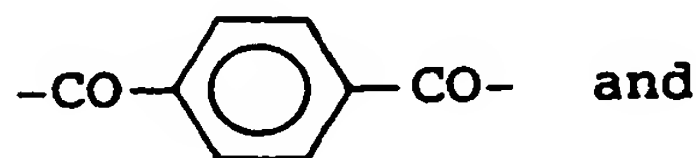
According to the present invention, there are provided a wholly aromatic polyester resin composition comprising:

(1) 40-79.5% by weight of a wholly aromatic polyester resin having:

(A) at least one repeating unit selected from the group consisting of:

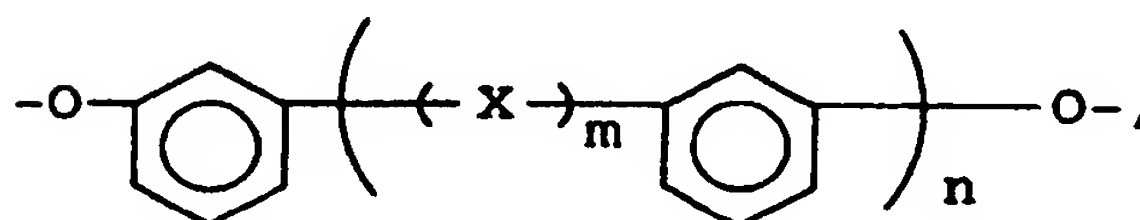
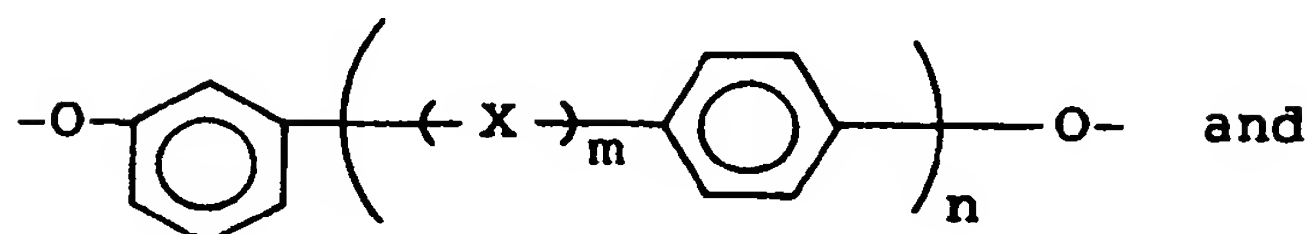
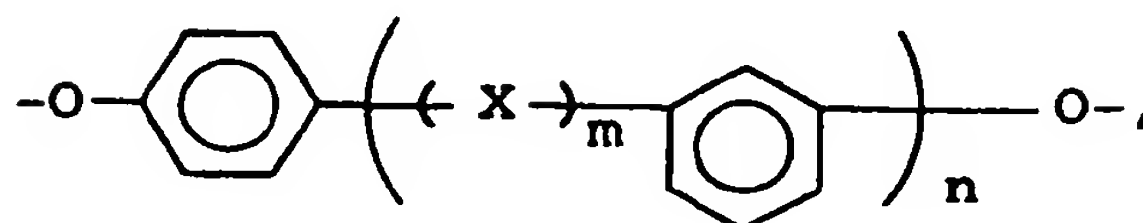
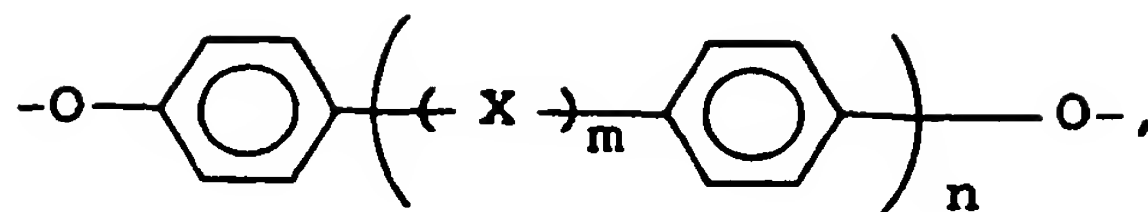


(B) at least one repeating unit selected from the group consisting of:



and

(C) at least one repeating unit selected from the group consisting of:



wherein X is -O-, -SO<sub>2</sub>-, -S- or -CO-, and m and n are independently 0 or 1,

wherein the numerical ratio of the repeating unit (A) to the repeating unit (B) ranges from 1 : 1 to 10 : 1, and the numerical ratio of the repeating unit (B) to the repeating unit (C) ranges from 9 : 10 to 10 : 9,

(2) 5-25% by weight of at least one fibrous reinforcing agent selected from the group consisting of a glass fiber and a silica-alumina fiber,

(3) 10-40% by weight of glass beads,

(4) 5-25% by weight of titanium oxide, and

(5) 0.5-10% by weight of fluorocarbon polymer with totally fluorinated terminals which polymer gives a flow temperature of 350° C or below when the flow temperature is defined as a temperature at which the polymer melted by heating at a temperature elevation rate of 4° C/min gives a melt viscosity of 48,000 poises when extruded through a nozzle of 1 mm in inside diameter and 10 mm in length under a load of 100 kg/cm<sup>2</sup>, using a capillary rheometer having said nozzle, the total content of the components (2) to (5) in the composition falling within the range of 20.5-60% by weight; and an overware obtained by molding the wholly aromatic polyester resin composition.

Specific examples of the comonomers of the wholly aromatic polyester used in the present invention are parahydroxybenzoic acid, metahydroxybenzoic acid, terephthalic acid, isophthalic acid, hydroquinone, resorcin, 4,4'-dihydroxydiphenyl, 4,4'-dihydroxydiphenyl ether, 4,4'-dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenyl sulfide, 4,4'-dihydroxybenzophenone and their derivatives.

Of these, there are particularly preferred combinations of parahydroxybenzoic acid or its ester, terephthalic acid, isophthalic acid or its ester, and 4,4'-dihydroxydiphenyl or its ester. In obtaining a wholly aromatic polyester from these components, it is possible to employ processes disclosed in USP 4,327,205, JP-A-57-44622, etc.; however, other processes can be used as well.

The glass fiber used in the present invention is a glass fiber generally used as a reinforcing agent for resins. These can be used a short fiber of 50-250 μm in number-average fiber length (so-called milled glass fiber) or a long fiber of 2-5 mm in number-average fiber length (so-called chopped glass fiber); however, a milled glass fiber is preferable in view of the appearance of molded article. A milled glass fiber having a

number-average fiber diameter of 10  $\mu\text{m}$  or less is particularly preferable. Examples of the commercially available milled glass fiber include EFH 75-01 and EFDE-50-01 (these are products of Central Glass Fiber Co., Ltd.) and REV-8 (a product of Nippon Glass Fiber Co., Ltd.).

The silica-alumina fiber used in the present invention contains silica and alumina as main components. Those of various compositions are commercially available under a popular name of ceramic fiber. They even include an alumina-based fiber using alumina as a main component and a silica-based fiber using silica as a main component.

A typical example of the silica-alumina fiber is a fiber obtained by electrically melting substantially equal amounts of high-purity silica and alumina and blowing off the fine streams of the melt with high pressure air to convert the streams to a fiber. This fiber has a number-average fiber length of 50-200  $\mu\text{m}$  and, as compared with a glass fiber, has a small number-average fiber diameter of 1.8-3.0  $\mu\text{m}$ , and has a high maximum use temperature of 1,260°C. Examples of the commercial products of such a fiber are Ibiwool® CP-U<sub>3</sub> and Ibiwool® CP-U<sub>11</sub> (these are products of IBIDEN CO., LTD.) and Kaowool® (a product of Isolite Insulating Products Co., Ltd.). An example of the commercial product of the alumina-based fiber is Saffil® (a product of ICI Japan, Limited).

The glass beads used in the present invention are those generally used as a filler for resins. Glass beads made of E-glass, having a weight-average diameter of 50  $\mu\text{m}$  or less are particularly preferable. An example of the commercial product is EGB 731 (a product of Toshiba Ballotini Co., Ltd.).

The fibrous reinforcing agent and glass beads can be used each in an untreated state. However, in order for them to have improved affinity with the resin, they may be used after being surface-treated with, for example, an aminosilane or epoxysilane coupling agent in such an extent that the object and effect of the present invention and not impaired.

The titanium oxide used in the present invention refers to TiO<sub>2</sub> widely used as a white pigment having a high hiding power. TiO<sub>2</sub> has two crystal structures, i.e. anatase type and rutile type. The anatase type is metastable and, at high temperatures, is converted to the rutile type which is stable. Moreover, the rutile type has a higher refractive index and a higher (by about 35%) hiding power than the anatase type. Therefore, the rutile type is preferable also in the present invention. TiO<sub>2</sub> of rutile type having weight-average particle diameters of 0.10-0.40  $\mu\text{m}$  is used generally. TiO<sub>2</sub> surface-treated with a hydrated oxide of Al, Si or the like or with an organic substance having good compatibility with the resin, can also be used as long as it does not adversely affect the thermal stability of the resulting composition. Examples of the commercial products of TiO<sub>2</sub> are Tipaque® CR-50, CR-60 and A-100 (these are products of ISHIHARA SANGYO KAISHA, LTD.) and KR 310 (a product of Titan Kogyo K.K.).

The wholly aromatic polyester resin composition of the present invention is preferably compounded so as to contain 40-79.5% by weight of the wholly aromatic polyester, 5-25% by weight of at least one fibrous reinforcing agent selected from the group consisting of the glass fiber and the silica-alumina fiber, 10-40% by weight of the glass beads, 5-25% by weight of the titanium oxide and 0.5-10% by weight of the fluorocarbon polymer with totally fluorinated terminals which polymer has a flow temperature of 350°C or below, with the total amount of the fibrous reinforcing agent, the glass beads, the titanium oxide and the fluorocarbon polymer being 20.5-60% by weight of the resin composition.

The resin composition of the present invention is more preferably compounded so as to contain 40-64% by weight of the wholly aromatic polyester, 10-20% by weight of at least one fibrous reinforcing agent selected from the group consisting of the glass fiber and the silica-alumina fiber, 20-30% by weight of the glass beads, 5-15% by weight of the titanium oxide and 1-5% by weight of the fluorocarbon polymer with totally fluorinated terminals and having a flow temperature of 350°C or below, with the total amount of the fibrous reinforcing agent, the glass beads, the titanium oxide and the fluorocarbon polymer being 36-60% by weight of the resin composition.

When the total amount of the fibrous reinforcing agent, the glass beads, the titanium oxide and the fluorocarbon polymer is more than 60% by weight of the resin composition and the amount of the wholly aromatic polymer is less than 40% by weight, the resulting composition has a poor melt flowability; therefore, its molding is difficult or, even if the molding is possible, the molded article is brittle and finds no practical use as an ovenware. Meanwhile, when the total amount of the fibrous reinforcing agent, the glass beads, the titanium oxide and the fluorocarbon polymer is less than 20.5% by weight, the resulting composition has no sufficient improvement in anisotropy and, when molded into an ovenware, gives warpage.

Even when the total amount of the fibrous reinforcing agent, the glass beads, the titanium oxide and the fluorocarbon polymer is 20.5-60% by weight of the resin composition, if the amount of the fibrous reinforcing agent is less than 5% by weight, the resulting composition has insufficient mechanical strengths; if the amount of the fibrous reinforcing agent is more than 25% by weight, the molded article obtained from



the resulting composition has poor appearance. Meanwhile, if the amount of the glass beads is less than 10% by weight, improvement in anisotropy is insufficient; if the amount of the glass beads is more than 40% by weight, reduction in mechanical strengths is large. Further, if the amount of the titanium oxide is less than 5% by weight, improvement in appearance is insufficient; if the amount is more than 25% by weight, the resulting composition has appearance similar to when the amount is 25% by weight or less, and has reduced mechanical strengths. If the amount of the fluorocarbon polymer is less than 0.5% by weight, improvement in releasability and non-tackiness is insufficient; if the amount is more than 10% by weight, reduction in mechanical strengths is incurred.

The fluorocarbon polymer used in the present invention is a low-molecular weight fluorocarbon polymer with totally fluorinated terminals which polymer has a flow temperature of 350°C or below when measured by the following method. The fluorocarbon polymer is preferably a polytetrafluoroethylene (hereinafter referred to as PTFE).

Flow temperature: a temperature at which a polymer melted by heating at a temperature elevation rate of 4°C/min gives a melt viscosity of 48,000 poises when extruded through a nozzle of 1 mm in inside diameter and 10 mm in length under a load of 100 kg/cm<sup>2</sup>, using a capillary rheometer having said nozzle.

The addition of the fluorocarbon polymer allows the resulting composition to have improved releasability from mold and further allows the ovenware molded from the composition to have excellent non-tackiness. With the addition of the fluorocarbon polymer, the composition further has excellent thermal stability and uniformity (dispersibility of the components).

As described in JP-A-61-118331 and JP-A-61-162503, the fluorocarbon polymer can be produced by catalytically reacting a fluorine-containing polymer with a nitrogen-containing fluorine compound at 250-550°C, or alternatively, by catalytically reacting said polymer at the same temperature with at least one substance selected from molecular fluorine, halogenated fluorides and rare gas fluorides. An example of the commercial product of the fluorocarbon polymer is Cefral Lube® I and IP (Products of Central Glass Co., Ltd.).

The composition of the present invention may further comprise at least one of ordinary additives such as antioxidant, heat stabilizer, ultraviolet absorber, coloring agents (e.g. dye, pigment) and the like, as long as the object of the present invention is not impaired. The addition of wollastonite is not preferable, because the ovenware molded from a composition containing wollastonite may cause dissolution of wollastonite in acetic acid.

The compounding means for obtaining the composition of the present invention has no particular restriction. In general practice, a wholly aromatic polyester, a fibrous reinforcing agent, glass beads, titanium oxide and a fluorocarbon polymer are mixed by a Henschell mixer, a tumbler or the like, and the mixture is melt kneaded by an extruder.

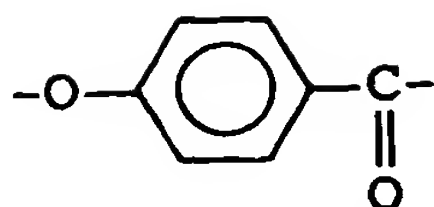
The composition of the present invention has high heat resistance and mechanical strengths, low anisotropy, excellent appearance, low dissolution in an extraction test according to No. 20 of the Welfare Ministry, excellent releasability and non-tackiness, and the vessels molded from the composition have properties suitable for use as ovenwares.

#### Examples

The present invention is hereinafter described in more detail by way of Examples. However, the present invention is in no way restricted to these Examples.

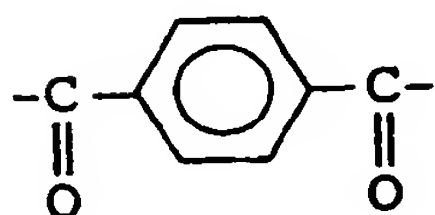
#### Reference Example 1 Production of wholly aromatic polyester A

Into a polymerization tank provided with comb-shaped agitating blades were fed 10.8 kg (60 moles) of p-acetoxybenzoic acid, 2.49 kg (15 moles) of terephthalic acid, 0.83 kg (5 moles) of isophthalic acid and 5.45 kg (20.2 moles) of 4,4'-diacetoxydiphenyl. The mixture was heated to 330°C and polymerized at that temperature for 1 hour with stirring in a nitrogen gas atmosphere. The polymerization was effected with vigorous stirring while removing acetic acid generated as a by-product. Then, the system was slowly cooled and the reaction mixture was taken out of the system at 200°C. The yield of the reaction mixture was 13.25 kg (97.8% of theoretical yield). The reaction mixture was ground with a hammer mill made by Hosokawa Micron K.K. to prepare particles of 2.5 mm or less. The particles were treated in a rotary kiln in a nitrogen gas atmosphere at 280°C for 3 hours to obtain a wholly aromatic polyester A in a particulate state, which comprised the following repeating units and had a flow temperature of 324°C. This polymer showed optical anisotropy at temperatures of 340°C or more under pressure.



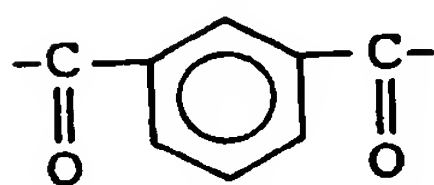
(A)

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(Bp)

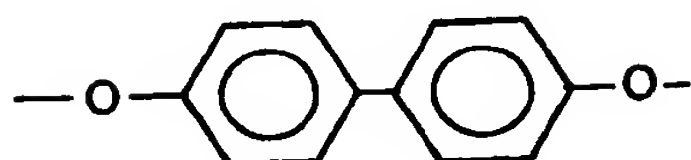
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(Bm)

15

20



(C)

25

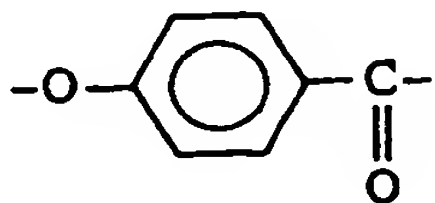
The numerical ratio of the repeating units (A), (Bp), (Bm) and (C) was 60 : 15 : 5 : 20.

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#### Reference Example 2 Production of wholly aromatic polyester B

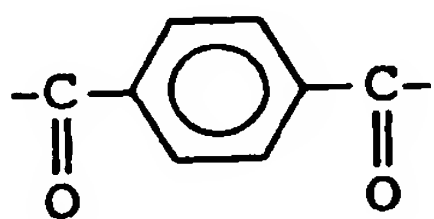
7.2 kg (40 moles) of p-acetoxybenzoic acid, 3.154 kg (19 moles) of terephthalic acid, 0.166 kg (1 mole) of isophthalic acid and 5.45 kg (20.2 moles) of 4,4'-diacetoxydiphenyl were polymerized under the same conditions as in Reference Example 1, to obtain a reaction mixture. The reaction mixture was ground in the same manner as in Reference Example 1 and then heat-treated in a rotary kiln in a nitrogen gas atmosphere at 280°C for 3 hours, followed by heat treatment at 325°C for 3 hours, to obtain a wholly aromatic polyester B in a particulate state, which comprised the following repeating units and had a flow temperature of 375°C. This polymer showed optical anisotropy at temperatures of 385°C or more under pressure.

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(A)

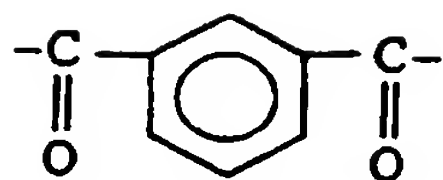
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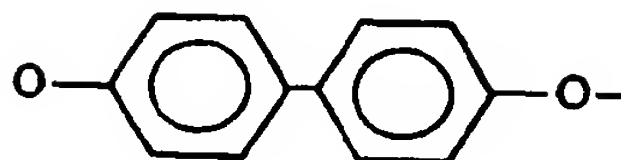
(Bp)

50

55



(Bm)



(C)

The numerical ratio of the repeating units (A), (Bp), (Bm) and (C) was 40 : 19 : 1 : 20.

In the above Reference Examples, flow temperature and optical anisotropy were measured in accordance with the following methods.

#### (1) Flow temperature

This was measured by a Koka type flow tester (CFT-500 manufactured by Shimadzu Corp). It is a temperature at which a resin melted by heating at a temperature elevation rate of 4°C/min shows a melt viscosity of 48,000 poises when extruded through a nozzle of 1 mm in inside diameter and 10 mm in length under a load of 100 kg/cm<sup>2</sup>. A resin of lower flow temperature has higher flowability.

#### (2) Optical anisotropy

The optical anisotropy of a resin in a molten state was measured by heating a powdery resin placed on a heating stage, at a rate of 10°C/min under a polarized light and making visual observation. When there occurred no complete melting when the resin was allowed to stand, a spring pressure was applied.

#### Comparative Example 1

The wholly aromatic polyester A, a glass fiber (EFDE 50-01 manufactured by Central Glass Co., Ltd.) of 6 μm in number-average diameter and 50 μm in number-average length, glass beads (EGB 731 manufactured by Toshiba Ballotini Co., Ltd.) of 17 μm in weight-average diameter and titanium oxide (CR-60 manufactured by ISHIHARA SANGYO KAISHA, LTD.) were mixed according to a composition shown in Table 1. The mixture was melt kneaded at a temperature of 340°C using a twin-screw extruder (PCM-30 manufactured by Ikegai Iron Works, Ltd.) to obtain pellets. The pellets were subjected to molding at a cylinder temperature of 350°C and a mold temperature of 130°C using an injection molding machine (PS40E 5ASE manufactured by Nissei Jushi Kogyo K.K.), to obtain a test piece (64 mm square and 3 mm thickness) for measurement of mold shrinkage, an ASTM No. 4 dumbbell for tensile test, and a test piece [127 mm (length) x 12.7 mm (width) x 6.4 mm (thickness)] for measurement of heat distortion temperature (HDT). Mold shrinkage was obtained by measuring MD and TD; tensile strength and HDT were measured in accordance with ASTM D 638 and ASTM D 648, respectively. Izod impact strength (unnotched) was measured in accordance with ASTM D 256, by dividing the test piece for HDT measurement into two equal portions in the lengthwise direction. The results are shown in Table 1.

#### Comparative Example 2

The composition of Comparative Example 1 was subjected to injection molding using an injection molding machine (515/150 MS manufactured by Mitsubishi Heavy Industries, Ltd.), at a cylinder temperature of 340°C and a mold temperature of 180°C to obtain a vessel of 148 mm x 104 mm x 32 mm (depth) (wall thickness: 1.6-2.0 mm). The vessel had good appearance and no warpage.

The vessel obtained in Comparative Example 2 and the test piece for measurement of mold shrinkage obtained in Comparative Example 1 were measured for dropping impact resistance, resistance to the use in a microwave oven with electric range, property not to contaminate food and extraction test according to No. 20 of the Welfare Ministry, according to the following methods. The results are shown in Table 2.

#### (1) Dropping impact resistance



An empty vessel was dropped on a plastic tile from a height of 1.5 m and there was examined the times of dropping until the vessel showed first cracking. When there occurred no cracking after 20 times of dropping, it was expressed as >20.

5 (2) Resistance to the use in a microwave oven with electric range

An empty vessel was placed on the turn table of a microwave oven with electric range (NE-8300 manufactured by Matsushita Electric Industrial Co., Ltd.) and irradiated with a microwave for 10 minutes. Then, the vessel was heated to 250°C by the 600 W electric range of the oven and kept at that  
10 temperature for 10 minutes. The vessel was then taken out and examined for dimension and appearance.

(3) Property not to contaminate food

50 cc of a soy sauce was placed in a vessel; the vessel was placed on the turn table of a microwave  
15 oven with electric range (NE-8300 manufactured by Matsushita Electric Industrial Co., Ltd.) and irradiated with a microwave for 15 minutes; then, the vessel was washed. This cycle was repeated five times, after which the appearance of the resulting vessel was examined.

(4) Extraction test according to No. 20 of the Welfare Ministry

20 A test piece for measurement of mold shrinkage was immersed in a 4% aqueous acetic acid solution at 121°C for 120 minutes; the resulting solution was subjected to evaporation; the amount of evaporation residue was weighed and expressed as dissolution amount.

25 Comparative Example 3

A composition corresponding to that of Comparative Example 1 were prepared by using the wholly aromatic polyester B in place of the wholly aromatic polyester A, and measured for properties. Melt kneading and injection molding were conducted in the same manner as in Comparative Example 1 except  
30 that the temperature of melt kneading by twin-screw extruder was 370°C and the cylinder temperature in injection molding was 400°C.

The results are shown in Table 3.

A vessel was molded from the composition of Comparative Example 3 in the same manner as in Comparative Example 2. It had good appearance and no warpage. This vessel and the test piece for  
35 measurement of mold shrinkage obtained in Comparative Example 3 showed the same results as in Comparative Examples 1 and 2, in dropping impact resistance, resistance to the use in a microwave oven with electric range, property not to contaminate food and extraction test according to No. 20 of the Welfare Ministry.

40 Examples 1 and 2

3 Parts by weight of a PTFE with totally fluorinated terminals which PTFE had a flow temperature of 318°C (Cefral Lube® I manufactured by Central Glass Co., Ltd.), was added to each of 100 parts by weight of the composition of Comparative Example 1 (composition of the components: wholly aromatic polyester  
45 A:glass fiber:glass beads:titanium oxide = 50:15:25:10 by weight) and 100 parts by weight of the composition of Comparative Example 3 (composition of the components: wholly aromatic polyester B:glass fiber:glass beads:titanium oxide = 50:15:25:10 by weight). Each of the resulting mixtures were melt-kneaded and injection-molded in the same manner as in Comparative Example 1 or 3, followed by measurements of mold shrinkage, tensile strength, Izod impact strength and HDT and observation of  
50 appearance of molded article. The results are shown in Table 4.

Comparison of Example 1 and Comparative Example 1 and Comparison of Example 2 and Comparative Example 3 indicated that the addition of PTFE gave slight reduction in tensile strength and HDT and slight improvement in Izod impact strength. The addition gave substantially no change in mold shrinkage.

55 Example 3

The compositions of Example 1 and Example 2 each containing a PTFE were molded into vessels in the same manner as in Comparative Example 2. Releasability from mold was good in each case, and the

vessels had good appearance and no warpage.

The vessels and the compositions of Example 1 and Example 2 were measured for dropping impact resistance, resistance to the use in a microwave oven with electric range, property not to contaminate food and extraction test according to No. 20 of the Welfare Ministry. The results were similar to those of Comparative Example 3.

25 Grams of a soy sauce was placed in each of the above vessels and in the vessels obtained from the compositions of Comparative Example 1 and Comparative Example 3; each vessel was then placed on the turn table of a microwave oven with electric range (RE-HL10 manufactured by Sharp Corp.) and heated at 250° C for 10 minutes by the electric range; thereafter, the vessel was washed. This cycle was repeated five times, after which the appearance of the vessel was examined. In the vessels obtained from the compositions of Example 1 and Example 2 containing a PTFE, the scorch of the soy sauce stuck to the surface after heating but was removed by the washing, and there was substantially no coloring even after the fifth cycle.

Meanwhile, in the vessels obtained from the compositions of Comparative Example 1 and Comparative Example 3 each containing no PTFE, the scorch was not removed completely by the washing and slight coloring was seen already in the first cycle.

The same results as above were obtained also when the soy sauce was replaced by a Worcester sauce or a curry sauce.

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Table 1

|                       | Composition (wt.%)        |                           |             |                | Mold shrinkage (%) |      |
|-----------------------|---------------------------|---------------------------|-------------|----------------|--------------------|------|
|                       | Wholly aromatic polymer A | Fibrous reinforcing agent | Glass beads | Titanium oxide | MD                 | TD   |
| Comparative Example 1 | 50                        | 15 (glass-fiber)          | 25          | 10             | 0.26               | 0.92 |

- to be cont'd -

Table 1 (cont'd)

| Tensile strength (kg/cm <sup>2</sup> ) | Izod impact strength (kg·cm/cm) | HDT (°C) | Appearance of molded article |
|--|---------------------------------|----------|------------------------------|
| 960                                    | 16                              | 270      | Good                         |

Table 2

|                     |                                      |                            |   |                       |  |
|---------------------|--------------------------------------|----------------------------|---|-----------------------|--|
| Kind of composition | Composition of Comparative Example 1 | Dropping impact resistance | Resistance to the use in a microwave oven with electric range | Contamination to food | Dissolution amount (ppm) according to No. 20 of the Melfare Ministry |
|                     |                                      | >20                        | No abnormality found  | No abnormality found  | 22.5   |

Table 3

|                       | Composition (wt.%)        |                           |             |                | Mold shrinkage (%) |      |
|-----------------------|---------------------------|---------------------------|-------------|----------------|--------------------|------|
|                       | Wholly aromatic polymer B | Fibrous reinforcing agent | Glass beads | Titanium oxide | MD                 | TD   |
| Comparative Example 3 | 50                        | 15 (glass-fiber)          | 25          | 10             | 0.23               | 0.94 |

- to be cont'd -

Table 3 (cont'd)

| Tensile strength (kg/cm <sup>2</sup> ) | Izod impact strength (kg·cm/cm) | HDT (°C) | Appearance of molded article |
|--|---------------------------------|----------|------------------------------|
| 980                                    | 17                              | 345      | Good                         |



Table 4

|           | Composition  | Mold shrinkage (%) |      |
|-----------|--|--------------------|------|
|           |  | MD                 | TD   |
| Example 1 | 3 Parts by weight of a PTFE was added to 100 parts by weight of the composition of Comparative Example 1 | 0.26               | 0.90 |
| Example 2 | 3 Parts by weight of a PTFE was added to 100 parts by weight of the composition of Comparative Example 3 | 0.22               | 0.91 |

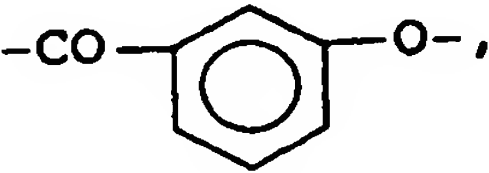
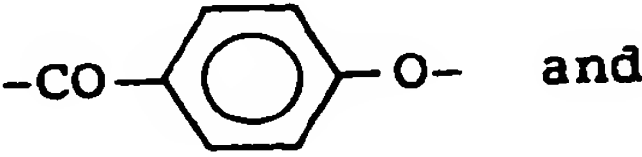
- to be cont'd -

Table 4 (cont'd)

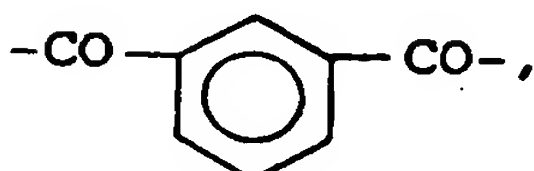
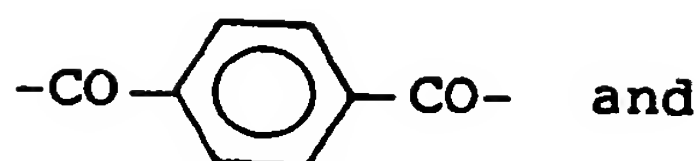
| Tensile strength<br>(kg/cm <sup>2</sup> ) | Izod impact strength<br>(kg·cm/cm) | HDT (°C) | Appearance of molded article |
|---|------------------------------------|----------|------------------------------|
| 920                                       | 25                                 | 266      | Good                         |
| 930                                       | 22                                 | 339      | Good                         |

Claims

1. A wholly aromatic polyester resin composition comprising:  
(1) 40-79.5% by weight of a wholly aromatic polyester resin having:  
(A) at least one repeating unit selected from the group consisting of:

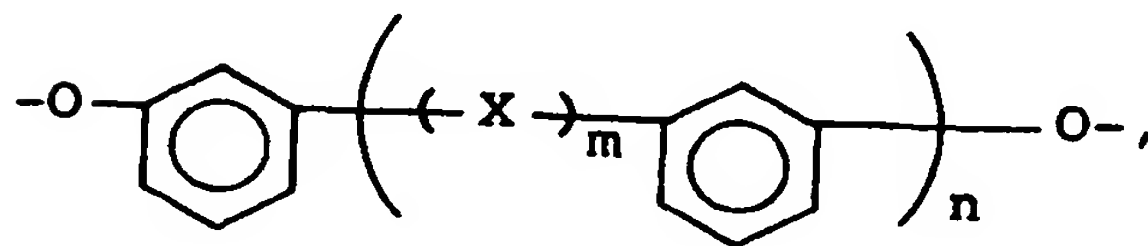
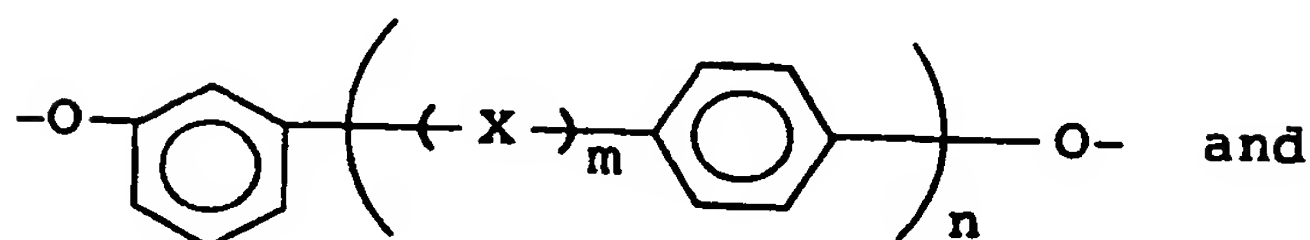
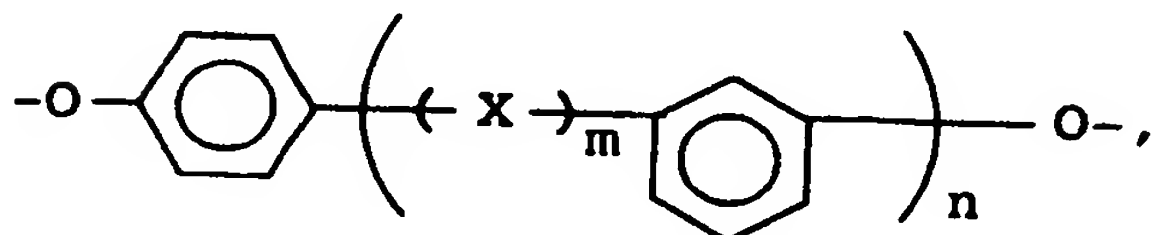
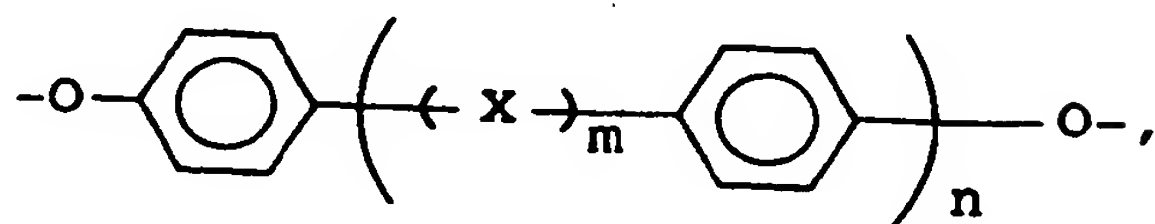


- (B) at least one repeating unit selected from the group consisting of:



and

(C) at least one repeating unit selected from the group consisting of:



wherein X is -O-, -SO<sub>2</sub>-, -S- or -CO-, and m and n are independently 0 or 1,

wherein the numerical ratio of the repeating unit (A) to the repeating unit (B) ranges from 1 : 1 to 10 : 1, and the numerical ratio of the repeating unit (B) to the repeating unit (C) ranges from 9 :

10 to 10 : 9,

(2) 5-25% by weight of at least one fibrous reinforcing agent selected from the group consisting of a glass fiber and a silica-alumina fiber,

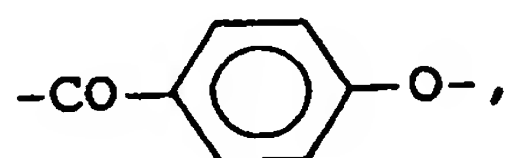
(3) 10-40% by weight of glass beads,

(4) 5-25% by weight of titanium oxide, and

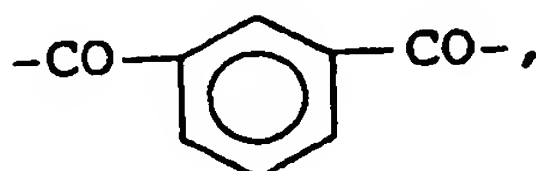
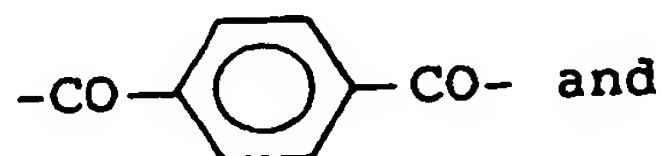
(5) 0.5-10% by weight of fluorocarbon polymer with totally fluorinated terminals which polymer gives a flow temperature of 350°C or below when the flow temperature is defined as a temperature at which the polymer melted by heating at a temperature elevation rate of 4°C/min gives a melt viscosity of 48,000 poises when extruded through a nozzle of 1 mm in inside diameter and 10 mm in length under a load of 100 kg/cm<sup>2</sup>, using a capillary rheometer having said nozzle, the total content

of the components (2) to (5) in the composition falling within the range of 20.5-60% by weight.

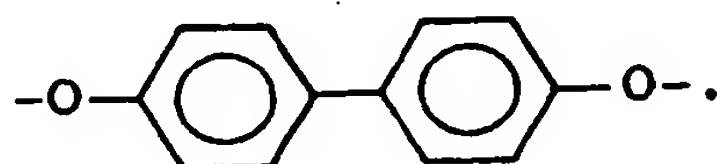
2. The wholly aromatic polyester resin composition of claim 1, wherein the repeating unit (A) is



the repeating unit (B) is



and the repeating unit (C) is



3. The wholly aromatic polyester resin composition of claim 1, wherein the fibrous reinforcing agent is a glass fiber.
4. The wholly aromatic polyester resin composition of claim 3, wherein the glass fiber has a number-average fiber length of 50-250  $\mu\text{m}$  and a number-average fiber diameter of 10  $\mu\text{m}$  or less.
5. The wholly aromatic polyester resin composition of claim 1, wherein the fibrous reinforcing agent is a silica-alumina fiber.
6. The wholly aromatic polyester resin composition of claim 5, wherein the silica-alumina fiber has a number-average fiber length of 50-200  $\mu\text{m}$  and a number-average fiber diameter of 1.8-3.0  $\mu\text{m}$ .
7. The wholly aromatic polyester resin composition of claim 1, wherein the glass beads have a weight-average diameter of 50  $\mu\text{m}$  or less.
8. The wholly aromatic polyester resin composition of claim 1, wherein the titanium oxide is a rutile type and has a weight-average particle diameter of 0.10-0.40  $\mu\text{m}$ .
9. The wholly aromatic polyester resin composition of claim 1, wherein the fluorocarbon polymer is a polytetrafluoroethylene.
10. The wholly aromatic polyester resin composition of claim 1, which is wollastonite-free.

11. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 1.
12. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 2.
- 5 13. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 4.
14. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 6.
- 10 15. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 7.
16. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 8.
17. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 9.
- 15 18. An ovenware obtained by molding the wholly aromatic polyester resin composition of claim 10.

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(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) Publication number:

**0 494 422 A3**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **91121842.8**

(51) Int. Cl.<sup>5</sup>: **C08L 67/00, C08K 13/04,  
A47J 36/04, //(C08L67/00,27:18)**

(22) Date of filing: **19.12.91**

(30) Priority: **08.01.91 JP 435/91**

(43) Date of publication of application:  
**15.07.92 Bulletin 92/29**

(84) Designated Contracting States:  
**DE FR GB NL**

(88) Date of deferred publication of the search report:  
**21.10.92 Bulletin 92/43**

(71) Applicant: **SUMITOMO CHEMICAL COMPANY,  
LIMITED**  
**5-33, Kitahama 4-chome Chuo-ku  
Osaka(JP)**

(72) Inventor: **Asai, Kuniaki**  
**8-8, Tanigawacho**  
**Tondabayashi-shi(JP)**  
Inventor: **Kobayashi, Tadayasu**  
**12-19-206, Ninomiya-1-chome**  
**Tsukuba-shi(JP)**  
Inventor: **Maeda, Mituo**  
**40-1, Kasuga-2-chome**  
**Tsukuba-shi(JP)**

(74) Representative: **Henkel, Feiler, Hänzel &  
Partner**  
**Möhlstrasse 37**  
**W-8000 München 80(DE)**

(54) **Wholly aromatic polyester resin composition and ovenware obtained by moulding said composition.**

(57) **A wholly aromatic polyester resin composition contains:**

- (1) a wholly aromatic polyester resin,
- (2) at least one member selected from a glass fiber and a silica-alumina fiber,
- (3) glass beads,
- (4) titanium oxide, and
- (5) a fluorocarbon polymer.

The wholly aromatic polyester resin composition has high heat resistance and mechanical strengths, low anisotropy and excellent appearance, and shows low dissolution of components, excellent releasability and non-tackiness. It can be molded into an ovenware.

EP 0 494 422 A3



European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 91 12 1842

| DOCUMENTS CONSIDERED TO BE RELEVANT   |   |   |   |
|---|---|---|---|
| Category  | Citation of document with indication, where appropriate, of relevant passages   | Relevant to claim   | CLASSIFICATION OF THE APPLICATION (Int. Cl.5)                 |
| P,X   | EP-A-0 446 803 (SUMITOMO CHEMICAL COMPANY LTD)<br>* page 5, line 41 - line 45 *<br>* claims *<br>* examples *<br>* page 4, line 41 - page 5, line 23 *<br>--- | 1-18  | C08L67/00<br>C08K13/04<br>A47J36/04<br>/(C08L67/00,<br>27:18) |
| A   | WO-A-9 003 992 (AMOCO CORPORATION)<br>* claims 1-2,12,25 *<br>---   | 1-18  |   |
| A   | EP-A-0 199 020 (SUMITOMO CHEMICAL COMPANY LTD)<br>* claims *<br>---   | 1-18  |   |
| A   | EP-A-0 132 094 (SUMITOMO CHEMICAL COMPANY LTD)<br>* claims *<br>* page 6, line 28 - page 7, line 25 *<br>---  | 1   |   |
| A   | US-A-3 671 487 (VISVALDIS ABOLINS)<br>* claims 1,17 *<br>-----  | 1   |   |
|   |   |   | TECHNICAL FIELDS SEARCHED (Int. Cl.5)                         |
|   |   |   | C08L<br>C08K  |
| The present search report has been drawn up for all claims  |   |   |   |
| Place of search<br>THE HAGUE  |   | Date of completion of the search<br>28 AUGUST 1992  | Examiner<br>PERSSON E. K.                                     |
| CATEGORY OF CITED DOCUMENTS   |   |   |   |
| X : particularly relevant if taken alone<br>Y : particularly relevant if combined with another document of the same category<br>A : technological background<br>O : non-written disclosure<br>P : intermediate document |   | T : theory or principle underlying the invention<br>E : earlier patent document, but published on, or after the filing date<br>D : document cited in the application<br>L : document cited for other reasons<br>.....<br>& : member of the same patent family, corresponding document |   |

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